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Method for Producing and/or Selective Solid Catalysts from

Inorganic or Organometallic Materials

[Verfahren zur Herstellung Aktiver und/oder selektiver

Feststoff-katalysatoren aus anorganischen oder

metallorganischen Stoffen]

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Process for the production of active and/or selective solid catalysts from inorganic or organometallic substances.

This invention relates to the process for the vast and economic development of solid catalyst for heterogeneously catalyzed reaction, such as they are encountered during the processes in chemical production or in refinery technology as well as in environmental technology, by virtue of the parallelized examination after new evolutionary methods.

The development of new or improved heterogeneous inorganic solids catalysts is based on empirical expert knowledge and basic knowledge. There is comprehensive basic knowledge regarding the way in which individual inorganic components or compounds work during the catalysis of certain reaction substeps; this knowledge is highly significant in the development of catalysts; nevertheless, in practical terms, and for the foreseeable future, we cannot get along without producing a large number of catalysts that consists of various active components or phases and they have to be checked for their catalytic _____

[1]Numbers in the margin indicate pagination in the foreign text

effect in regard to the particular reaction.

As a rule, there will be several catalytically active phases for the performances of a predetermined reaction; these phases are produced in a suitable manner and within a ratio of active components that is to be determined empirically and in the process, they are brought together. The knowledge of the physical, physical-chemical and catalytic properties of solids constitutes a rational phase for the selection of catalytically effective material in connection with catalyst development and improvement. Even if in the ideal case, the correct individual components or individual phases of the catalyst can be selected, it is nevertheless required to determine the suitable mass ratio and preparation methods.

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A suitable procedure as such optimization problems involves the use of combinatory and evolutionary methods (Ugi, I. et al, Chimia 51 (1997) 39-44). These algorithms have so far been used in biochemistry and active substance research in the shortest possible time, to discover new substances with a desired specific effect from a large number of compounds.

These basic principles are in the mean time also used in the development of homogeneous catalysts (DE-A 197319904). The investigative substances are always dissolved in connection with the mentioned uses. The action range of the desired quality (for example catalytic activity and selectivity) is confined to

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one molecule whose optimum elementary composition and structure is wanted.

In contrast, as regard to heterogeneous catalysis, it is important to select the catalytically most effective inorganic solid materials and to determine their optimum mass shares in the final catalyst. By using new strategy in the development of heterogeneous catalyst, the idea is - compared to the methods that are in practice today are still mostly empirically oriented - on the one hand to reduce the experimental effort connected with catalytic development and on the other hand, to increase the probability of finding an optimum catalyst.

Combinatorics is an effective development strategy when a large number of parameters influence the properties of products. In spite of the great successes achieved with this strategy during the development of new medications, the use of combinatory methods in inorganic chemistry and catalysis is a brand-new field. The first use of combinatory methods in the development of new solid materials was reported in 1995 by Schultz et al. Science, 268 (1995) 1738 and Science 270 (1995) 273). The author told that the solid libraries could be thoroughly checked out for supra-conductivity and magneto resistance. During the same year, libraries of complexes for the selective bonding of metal ions as well as of phosphine containing peptidic ligands were made for the Rh(I) catalyzed

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hydration of methyl-2-acetamidoacrylate into N-acetylalaninmethylether. /$\underline{3}$

Described was the synthesis of libraries that contain a large number (up to 26,000) of combinations of inorganic materials on a silicon matrix (E. Danielson et al., Nature 389 (1997) 944). This technology was tried out among other things with the help of the example of the heterogeneous catalyzed CO oxidation to determine catalytically active solid materials. The results were illustrated in three-dimensional diagrams from which it was possible to determine the combinations that led to high CO_2 yields and thus the highest catalyst activity.

Also, described was a synthesis of a library of polyoxymetallates with a keggin structure (C.L. Hill et al, J. Mol. Catal. A 114 (1996) 114); 39 homogeneously dissolved catalysts were made during the mixing of aqueous solutions of $Na_2MO_4 \cdot 2H_2O$, $NaVO_3$ and Na_2MPO_4 (M=W, Mo). The resultant solutions were used without any further treatments during the aerobic oxidation of tetrahydrothiophene into sulfoxide at 95°. The educt mixing and the product formation were determined by means of GLC analysis and were presented at three-dimensional "reaction history" (x-axis - Mo/W content; y-axis - v-content; z-axis - product yield). Comparable results were achieved in most catalysts; therefore, it was impossible to draw really any informational conclusions.

A combinatory strategy was pursued by Mallouk et al. (Fuel Cell Seminar: Orlando, Florida (1996) 686, during the development and optimization of alloys consists of three metals that are used as anode materials for the electro chemical oxidation of methanol. Five noble metals (Pt, Ru, Os, Rh and Pd) used to make libraries (9 arrays with 135 compositions). This work is an example of effective parallelized investigation.

Combinatory libraries on metal catalysts supported on Al_2O_3 (among others Bi, Cr, Co, Co, Ni, Pd) with 16 elements of a matrix were used by Willson et al. during the hydrogen oxidation reaction. The reactor was equipped with a special camera for in-situ IR thermography; the catalytic activity was therefore determined via the ignition temperatures. One disadvantage of the analysis method used in this work is represented by the fact that no data are available on product selectivity.

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Looking at the methods of combinatorics described so far and their use to determine active substances and optimized catalysts, one must perform very many syntheses for these target materials all of which are time-consuming and expensive.

The object of the invention therefore is to develop a process for the production of heterogeneous solid catalyst for a predetermined reaction with reduced effort where the combinatory

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preparations are complementary replaced by other optimum methods.

According to the invention, evolutionary principles such as crossing and mutations were used; in the process, one works with the stochastic modification of the catalyst make-up. These methods do not lead to a pure random search but - by means of the activity determined and the selectivity determined direction of the catalyst to be modified - it leads to a directed optimalization that quickly and in a parallel fashion concentrates on several promising areas of the catalyst composition.

Here is the procedure according to the invention:

(i) production of substance libraries from individual catalytic materials and their mixtures;

(ii) testing materials - in other words individual materials and their mixtures from these substance libraries - for their catalytic operating procedures;

(iii) determination of chemical structure of catalytically active materials;

(iv) building on the knowledge gained according to (ii) and (iii) there is an iterative repetition of steps (i) to (iii) or to (iv) with the goal of catalyst optimalization.

This procedure can during the development of heterogeneous catalyst be implemented or translated into practice as follows:

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In the first step (i), primary components (individual materials or catalytically active phases) that were already described for the individual reaction steps of the considered heterogeneously catalyzed reaction or that are known or that were determined empirically or intuitively are selected and incorporated to the substance library; in the process, arbitrary mixtures of these individual materials are made by way of random selection.

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In the second step of (ii), these materials, that are so definitely determined and made (1st generation of catalyst are thoroughly tested catalytically) for example activity, field activity, space-time yield; these two procedures that is to say, productions and thorough testing, were in each case performed in as extensively parallelized manner as possible. The materials involved in step (ii) that are successive in terms of catalyst optimizing, are characterized especially with a view to their reproducible production in step (iii) in physical and physical-chemical terms, and represent the foundation for a following 2nd generation of catalysts. This 2nd generation is produced according to methods of biological evolution from the successive materials of the 1st generation and can then be subjected to steps (ii) and (iii).

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By methods of biological evolution, we mean here crossing and mutation. Here, by means of stochastic procedures such as random generators, casting dice, drawings, one performs a change in the catalysts components and/or quantitative shares of one or several catalysts of a selective pool of catalysts of the prior generation by means of arbitrary and/or random new structuring.

During the second and subsequent iterations, the most successive catalysts of all generations are in each case used as bases and their total number, when compared to the total number of catalyst of one generation however is generally small; as a rule it will amount to between one and 50% of the catalyst of one generation.

The iterations described are continued until such time as no further improvement of the catalytic behavior of the materials can be ascertained regarding the activity and/or selectivity for the particular reaction under consideration.

The method for the selection of components for the production of active and/or selected solid catalysts from inorganic or organometallic substances or mixtures thereof advantageously consists of the following steps where (a) for a catalytic reaction, one produces a number n_1 if solid catalyst from the elements of Periodic System of Elements (PSE) in the form of Formula (I) compounds.

$$(A^l_{a_l} .. A^i_{a_i})\text{-}(B^l_{b_l} .. B^j_{b_j})\text{-}(D^l_{d_l} .. D^k_{d_k})\text{-}(T^l_{t_l} .. T^l_{t_l})\text{-}O_p \qquad (I)$$

where A^1 . . A^i are various main components that are selected form the elements of the PSE excepting the transuranes and noble gases, preferably from the group of

Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce und Nd ausge-

[und = and] and where the number is between 1 and 10.

B^1 . . B^j are various secondary components that are selected from the group of elements:

Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce und Nd ausgewählt werden, und die Anzahl j zwischen 1 und 10 liegt,

and Nd and the number for j is between 1 and 10,

D^1 . . D^k k are various doping elements that different from the group of the following elements

Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce und Nd ausgewählt werden, und die Anzahl k zwischen 1 und 10 liegt,

and Nd and the number for k is between 1 and 10,

T^1 . . T^1 l are various carriers components that consists of oxides, carbonates, carbides, nitrides, borides, of the elements Mg, Ca, Sr, Ba, La, Zr, Ce, Al, Si or a mix phase of two or

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several thereof and the number for l is between 1 and 10 and O

is oxygen,

a_1 . . a_i are equal or different substance quantity portions from

0 to 100% by mol with the proviso at the substance quantity

portions a_1 . . a_i cannot all simultaneously be 0, b_1 . . b_j are

substance quantity shares of 0 to 90% by mol preferably 0 to 50%

by mol,

d_1 . . d_k are substance quantity shares of 0 to 10% by mol,

t_1 . . t_l are substance quantity shares of 0 to 99.99% by mol,

p is a substance quantity share of 0 to 75% by mol where the sum

of all substance quantity shares $a_i + b_j + d_k + t_l$ must not be

greater of 100% and the number n_1 of catalyst, composed

quantitatively and/or chemically in different ways is in the

range of 5 to 100,000 but preferably in the range of 5 to 100;

(b)   the activity or selectivity of the n_1 solid catalyst of

the 1st generation made according to (a) for a catalytic

reaction, where determined experimentally in a reactor or in

several parallel connected reactors;

(c)   from the number of n_1 catalyst of the 1st generation,

one selects a number of 1 - 50% with the highest activities for

a specific reaction and/or the highest selectivities for the

desired product or product mixture of the catalytic reaction as the number n_2 contained in the number n_2 of catalysts with a determined probability W, that results for each of the components A^1 . . A^i, B^1 . . B^j, D^1 . . D^k, and T^1 . . T^l results from the corresponding equations

$$W_A = \frac{1}{i \cdot n_2} \cdot 100\%, W_B = \frac{1}{j \cdot n_2} \cdot 100\%, W_D = \frac{1}{k \cdot n_2} \cdot 100\%, W_T = \frac{1}{l \cdot n_2} \cdot 100\%$$

between 2 each with a probability of

$$W_{Kat} = \frac{1}{n_2} \cdot 100\%$$

are exchanged from the quantity n_2 of selected catalysts and/or that the substance quantities a_1 . . a_i , b_1 . . b_j , d_1 . . d_k, and t_1 . . t_1 of the catalysts components A^1 . . A^i, B^1 . . B^j, D^1 . . D^k, and T^1 . . T^1 are varied for some of the catalyst that are selected with the probability:

$$W_{Kat} = \frac{1}{n_2} \cdot 100\%$$

. . . . in that new values are determined for the substance quantity shares, a_1 . . a_i , b_1 . . b_j , d_1 . . d_k, and t_1 . . t_1

within the boundaries defined in (a);

in this way, one can make new catalysts having the general formula (I) with the meanings given in (a) of A^1 . . A^i, B^1 . . B^j, D^1 . . D^k, T^1 . . T^1 , a_1 . . a_i , b_1 . . b_j , d_1 . . d_k, and t_1 . . t_1 and p in a number y_2 that form the 2nd generation of catalysts;

(e) the activities and selectivities of the y_2 solid catalysts of the 2nd generation are experimentally determined for

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the same specific reaction as in (b) in one or several reactors;

(f) a number of n_3 solid catalysts of the 2nd generation that display the highest activities from the catalytic mixing and/or the highest activities for the desired product and product mixture from all solid catalysts of the 1st and 2nd generation, are selected, while the number $-n_3$ corresponds to 1 to 50% of the number n_1 ;

(g) the catalysts components contained in the n_3 of catalysts, with a determined probability W that results for each component A^1 . . A^i, B^1 . . B^j, D^1 . . D^k, and T^1 . . T^l from the corresponding equation:

$$W_A = \frac{1}{i \cdot n_3} \cdot 100\%, W_B = \frac{1}{j \cdot n_3} \cdot 100\%, W_D = \frac{1}{k \cdot n_3} \cdot 100\%, W_T = \frac{1}{l \cdot n_3} \cdot 100\%$$

are exchanged between 2 each catalysts selected from the quantity n_3 with the probability of

$W_{Kat} = \frac{1}{n_3} \cdot 100\%$ and/or that the substance quantities a_1 . . a_i , b_1 . .
b_j , d_1 . . d_k, and t_1 . . t_l of the catalysts components A^1 . . A^i,
B^1 . . B^j, D^1 . . D^k, and T^1 . . T^l are varied for some of the catalyst selected with the probability

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$$W_{Kat} = \frac{1}{n_3} \cdot 100\%$$

in that new values are picked for the substance

quantity shares $a_1 \, . \, . \, a_i$, $b_1 \, . \, . \, b_j$, $d_1 \, . \, . \, d_k$, and $t_1 \, . \, . \, t_1$

within the boundaries determined in (a);

in this way, one can make new catalysts having the general

formula (I), with the meaning given in (a) of $A^1 \, . \, . \, A^i$, $B^1 \, . \, .$

B^j, $D^1 \, . \, . \, D^k$, $T^1 \, . \, . \, T^1$, $a_1 \, . \, . \, a_i$, $b_1 \, . \, . \, b_j$, $d_1 \, . \, . \, d_k$, and $t_1 \, .$

$. \, t_1$ and P in a number y_3 that form the 3rd generation catalysts;

(h) the activity and/or selectivity of the y_3 new catalyst

of the 3rd generation, made according to (g), is/are determined

for the same specific reaction as (b) in one or several

reactors;

(i) one selects a number of n_{n+1} solid catalyst of the nth

generation that display the highest activities for the catalytic

mixing and/or the highest selectivities for the desired product

and product mixture from all solid catalysts of the 1st to the

nth generation, where the number n_{n+1} corresponds to 1 to 50% of

the number n_1;

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(j) the catalysts components contained in the number n_{n+1} of

catalysts, are exchanged with a determined probability W that

results for each of the components $A^1 \, . \, . \, A^i$, $B^1 \, . \, . \, B^j$, $D^1 \, . \, . \, D^k$,

and $T^1 \, . \, . \, T^1$ from the corresponding equations:

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$$W_A = \frac{1}{i \cdot n_{n+1}} \cdot 100\%, \quad W_B = \frac{1}{j \cdot n_{n+1}} \cdot 100\%, \quad W_D = \frac{1}{k \cdot n_{n+1}} \cdot 100\%, \quad W_T = \frac{1}{l \cdot n_{n+1}} \cdot 100\%$$

are exchanged between 2 each catalysts selected with a probability of

$$W_{Kat} = \frac{1}{n_{n+1}} \cdot 100\%$$

from the quantity n_{n+1} and/or the substance quantities $a_1 \ldots a_i$, $b_1 \ldots b_j$, $d_1 \ldots d_k$, and $t_1 \ldots t_l$ of the catalysts components $A^1 \ldots A^i$, $B^1 \ldots B^j$, $D^1 \ldots D^k$, and $T^1 \ldots T^l$ are varied for some of the catalysts selected with probability

$$W_{Kat} = \frac{1}{n_{n+1}} \cdot 100\%$$

in that new values are determined for the substance quantity portions $a_1 \ldots a_i$, $b_1 \ldots b_j$, $d_1 \ldots d_k$, and $t_1 \ldots t_l$

within the boundaries (a);

in this way, one can make new catalysts having the general formula (I), with the meaning given in (a) of $A^1 \ldots A^i$, $B^1 \ldots B^j$, $D^1 \ldots D^k$, $T^1 \ldots T^l$, $a_1 \ldots a_i$, $b_1 \ldots b_j$, $d_1 \ldots d_k$, and $t_1 \ldots t_l$ and p in a number y_{n+1} that will form the $(n+1)^{th}$ generation of catalysts;

(k) the activity or selectivity of the y_{n+1} catalysts of the $(n+1)^{th}$ generation made according to (g), is/are determined for the same reaction as in (b) in one or several reactors;

(l) the selection according to steps (c) + (f) + (i), the production of a new catalysts generation according to steps (d), (g), (j) and the activity/selectivity determination are

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continued according to steps (e) + (h) + (k) until one gets a catalysts generation where the activity and/or selectivity is/are not increased when compared to the preceding generation in terms of the arithmetic means or is/are no longer significantly increased (>1%).

The number of selections n_2, n_3 or n_{n+1} preferably corresponds to between 5 and 30% of the number n_1.

The exchange of catalysts or the variation of the substance quantities or the exchange and variation in sections (d), (g) and (j) is preferably performed by means of numerical random generator. Here one advantageously uses the program codes G05CAF, G05DYF, G05DZF or G05CCF by NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd, 1986) of a numerical random generator.

One can also use random generators that are freely available in the internet for those – such as "Numerical Recipes in FORTRAN, PASCAL or C" Cambridge University Press, or IMSL Libraries of FORTRAN compilers DIGITAL visual Fortran Professional Edition, that are commercially available as software. Other stochastic methods, such as casting dice or drawings can be used for this step.

Using such methods, one could for example in step (d) above, select several catalyst components and their

corresponding molar substance quantity shares could be exchanged between the previously selected catalysts components (crossing). By means of quantitative shares, that are altered from a finite value to zero or from zero to a finite value, one can also bring about an exchange of the individual catalysts components as such as means of crossing, as a result of which on the whole, one gets a new composition of the catalysts of the new generation. The catalysts components selected for example by means of random generator can also, by means of multiplication with factors that are either randomly determined or freely determined from the quantity of real numbers between zero and 10,000 can be reduced or enlarged (mutation) so that the new catalyst of the next catalyst generation of course contains the same components but the latter are present in another concentration and so that the ratios of the components among each other can also be changed.

In process (a) the number n_1 of catalysts that are differently composed in quantitative terms and/or in chemical terms, is in the range between 5 and 100.

Advantageously, the catalyst mixtures are made by mixing small solutions of the elements of component A^1 . . A^i, B^1 . . B^j, D^1 . . D^k, and T^1 . . T^1 and subsequent thermal

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treatment in the presence of a reactive or inert gas phase (hereafter referred to as tempering) or by joint precipitation

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of compounds that are difficult to dissolve and subsequent tempering or by impacting the carrier components T^1 . . T^1 with salt solution or gaseous compounds of components A^1 . . A^i, B^1 . . B^j, D^1 . . D^k and subsequent tempering while the used salts can be nitrates, sultates, phosphates, carbonates, halogenides, oxalates, carboxylates, or mixtures thereof or carbonyls, or acetylacetonates.

New catalyst mixtures second to nth generations can be made by mechanical mixtures of the produced solid catalysts of the particular preceding generations. Other advantageous embodiments consists in the following: the catalytic reaction is performed with liquid, evaporated, or gaseous reactants and the reactants are supplied for the catalytic reaction to several reactors and the product flow leaving the reactors, is separately analyzed for each individual reactor.

To perform the catalytic reaction, one preferably connects parallel to each other or one arranges in arrays between 5 and 1000 reactors, consisting of spaces with catalytically active material arranged therein, while the diameters of these spaces amount to 100 µm to 10 mm and the lengths are between 1 mm and 100 mm. Assuming a predetermined reactor length, the throughput of the reactants is so chosen that the desired degree of mixing is obtained.

As reactor, one can use a monolith with many parallel channels, that as selective can be closed off on the entry or exit by individually or larger number also during a catalytic reaction or a porous module, preferably with channels that run parallel in the direction of flow of the reaction mixture that can be closed as desired, on the entry or exit side individually or in a larger number also during a catalytic reaction.

Advantageously, the reactants are supplied to the above reactors for the catalytic reactions and the composition of the product flows leaving the reactors, is analyzed by a measurement probe while the measurement probe is guided in a two-dimensional fashion via the exit cross sections of all reactors or the reactors are moved in a two-dimensional manner with respect to the measurement probe and the part of the product flows, acquired by the measurement probe is supplied to the analyzer. As analyzer, one can use a gas chromatograph, a mass spectrometer, or some other gas or liquid mixture suitable for analysis.

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To the reaction mixture, one can add suitable indicators that display the presence of individual or several educts or products and that thus permit their analysis in the reactant mixture. The solid catalyst can then be produced from solids, solutions or dispersions.

The term "actively or selectively improved catalyst" as used in the above description means the following: the catalyst display improved values regarding their activity for their selectivity or with respect to both properties. This must be equated with the improvement of the space-time yield.

By "stochastic methods" we mean all procedures that are not strictly deterministic with a random component. The invention-based stochastic methods are finite and discreet procedures.

The invention will be explained in greater detail with the help of the enclosed drawing.

Figure 1 is a diagram showing the change of the yield of the particular best 5 catalysts during the first three generations of catalyst optimization according to example 1.

Figure 2 is a diagram as in figure 1 according to example 2.

The invention will be explained by the following examples. Example 1 involves the search for the optimum catalyst for the partial oxidation of propane into its oxide derivatives that comprise the sum of acroleine, acetic acid, and acrylic acid. Example 1

We demonstrate the selection and mixing of individual catalyst components that here are subdivided into main, secondary, doping, and carrier components as well as the

thorough testing and further improvement of the catalyst mixtures using evolutionary optimization strategies.

To begin with, 30 catalysts (Phase 1) then 10 catalysts (Phase II) and then finally another 10 catalysts (Phase III) consisting of main components, secondary components, doping components and carrier material were prepared with the goal of making propane for its oxygen derivative by means of oxidation with oxygen and to minimize the developing oxides CO and CO_2 (see step (a) above). The development of the procedure comprise of the following steps and led to the particular results mentioned.

1st Catalyst Generation

Step 1. The main components were selected from among the oxides of the elements V, Mo, Nb, Bi, P. The shares of the main components were varied between 0 and 50% by mol. The secondary components were selected from among the oxides of the elements Mn, Sb, Sn and B. The shares of the secondary components were varied between 0 and 50% by mol. The doping components were selected from among the oxides of the elements Cs as well as Fe or Co, either Ag or Cu and either Ga or In. The shares of the doping components were varied between 0 and 5% by mol. Pd was used as an additional doping component that was either not introduced or that was introduced with a substance quantity of 10^{-4} % by mol of Pd. Al_2O_3 was used as carrier component that was

either not contained in the catalyst or that was contained in a quantity of 50% by weight.

The sum of all mass or molar shares of the main, secondary, doping and carrier components always turns out to be 1%.

Step 2. The catalysts that were used for testing, were obtained according to the following production procedure: compounds (oxides, oxalates, or nitrates) of the elements mentioned in step 1, were dissolved or washed in a little bit of water, they were mixed with each other and the mixture was evaporated. The resultant solid was dried for 1 hour at 200°C and for 3 hours at 400°C, it was then intensively ground for 1 hour in a ball mill and it was tempered in air for 3 hours at 600°C.

Step 3. The catalyst compositions of the 1st generation obtained by means of the random generators G05DZf, G05CAF, G05DYF, and G05CCf of NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd, 1986) are compiled in Table 1.

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Step 4. The catalyst were checked out parallel in 6 quartz reactors (inside diameter 6mm) that have been placed in a heatable and coolable fluidized sand bed for thermostat control. Alternate configurations of parallel testing of the solid catalysts are possible according to the above description. The

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following standard experimental conditions were chosen for the testing of the catalyst:

$$T = 500°C, \; m_{Katalysator} = 1,0 \; g,$$

$$\dot{V}_{gesamt \; pro \; Reaktor} = 28 \; ml_{STP} \; min^{-1} \; mit \; \dot{V}_{C3H8} = 0,8 \; ml_{STP} \; min^{-1}, \; \dot{V}_{O2} = 5,6$$

$$ml_{STP} \; min^{-1}, \; \dot{V}_{H2O} = 12,0 \; ml_{STP} min^{-1}, \; \dot{V}_{Ar} = 21,6 \; ml_{STP}.min^{-1}.$$

KEY:

catalysator – catalyst

gesamt pro reactor – total per reactor

The catalysts were used for the reaction and were checked out regarding the sum of yields of acroleine and acrylic acid obtained under the mentioned experimental conditions (see step (b) above; also corresponds to this step in claim 2). The concentration of propane, propene, ethylene, of the developed oxygen derivatives as well as of CO and CO_2 was analyzed by means of gas chromatograph and mass spectrometer.

Step 5. Results from testing the first generation catalysts are compiled in the form of the sum of the yields of acroleine and acrylic acid in Table 1. One finds significant differences in the yields of the thirty tested catalysts. The 5 best catalysts (Numbers 4, 13, 17, 19, 21) with the exception of 13, all contain the carrier component. Among these best catalysts, one frequently furthermore finds Mo as main component and Sn as secondary components. Except for Fe as doping

component, however, all catalyst components used are still represented among the 5 best catalysts of the first generation.

2nd Catalyst Generation

Step 6. The 2nd Generation of catalysts was obtained in the following manner: first of all, the five catalysts numbers 4, 19, 21, 13 and 17 with a highest oxygenate yield were selected from the thirty previously tested ones (corresponding to 17% of the 1st generation of catalysts) (see step (c) above).

Step 7. The compositions of 10 new catalysts of the 2nd generation were obtained in the following manner.

a) From the main, secondary, doping and carrier

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components of the five best catalysts (table 1: Numbers 4, 19, 21, 13 and 17) 6 new combinations of main, secondary, doping and carrier components were formed (see step (d) above) in that for example, for the composition of catalyst number 1 of the second generation (Table 2) first of all, we selected catalyst number 17 (hereafter, catalyst number _=K [sic]) by means of ZGI-Best5 [by means of the numerical random generators G05DYF, G05DZF, G05CCF of NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd, 1986) from the 5 best catalysts] and thereafter, by means of ZG1 [with the help of the numerical random generators G05DYF, G05DZF, G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd, 1986)] the main component Bi

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of K 17. Then K 21 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1 the main component P of K 21. Thereafter K 4 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1, the secondary component Sn of K 4. Then K 21 was selected by means of ZG1-Best5 and then by means of ZG1 the secondary component B of K 21. then K 14 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1, the trace component Fe of K 14. Then K 19 (Table 1) was selected by means of ZG1-Best5 and then by means ZG1, the trace component Co of K 19. Then K 17 (Table 1) was selected by means of ZG1-Best5 and by means ZG1, the trace or doping components Cs and Pd of K 17. The components thus selected were combined with their original molar quantities into a new catalysts composition. In a similar manner, K 2, 3, 6, 7 and 8 of the second catalyst generation (Table 2) were obtained.

b) The molar shares of the main, secondary, and doping components of the two best catalysts are changed with the highest oxygenate yield (Table 1, Number 4 and 19) according to the above step (d) in that the components Mo, Nb, Sb, Sn, Co and Ga of K 4 of the first generation was selected by means of ZG1 and the molar quantitative shares of these selected components were stochastically altered by means of ZG2 [with the help of the numerical random generators G05CAF, G05DZF, G05CCF of NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd, 1986)].

Then the components Mo, Bi, P, Sn and Co of K 19 of the first generation were selected by means of ZG1 and the molar quantitative share of the selective components were changed stochastically by means of ZG2.

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We obtained K 4 and K 5 of the second generation (Table 2) in a similar manner we obtained K 9 and K 10 of the second generation. All of the total of 10 resultants new catalysts of the second generation were produced as described for those of the first generation (step 2).

Step 8. The procedure described in step 7 was used to determine ten new catalyst compositions, they were produced according to directions (see step 1) and they were tested parallel under standard conditions as described in step 4 (see step (e)). These new catalysts contain more Mo as main component and Sn as secondary component. P as secondary component and Co as doping component that occurred already with increased frequency in the best catalyst of the first generation are also more frequently represented in the new catalysts of the second generation.

3rd Catalyst Generation

Step 9. From the quantities of the first and second catalyst generations, we again selected the 5 catalysts that supplied the highest yields of oxygen derivatives (see above

step (f)). These are the catalysts of Table 1: Number 4, 19, 21 and from Table 2: numbers 2, 3. With the 10 new catalysts from the second generation, one initially does not achieve any higher yields than the best catalysts of the first generation. But the number 2 and 3 catalysts of the second generation displays the number 19 or 21 catalysts from the 3rd and 4th ranks (see also figure 1).

Step 10. The composition of two newly to be produced catalysts of the third generation was obtained in the following manner: we proceeded as described in step 7 with the five catalysts selected in step 9 (see table 3, see above step (g)). We therefore selected K 4 (Table 2) by means of ZG1-Best5 and then by means of ZG1, the main component Nb of K 4 (Table 2). Then K 21 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1, the main component P of K 21 (Table 1). Then K 3 (Table 2) was selected by means of ZG1-Best5 and then by means of ZG1, the trace component Fe of K 14. Then K 19 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1 doping component Co of K 3 (Table 2). Then K 4 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1, the doping component Ga of K 4. Then K 2 (Table 2) was selected by means of ZG1-Best5 and then by means of ZG1 the carrier component of K 2 (Table 2).

The components thus selected are combined with their original molar quantities to form a new catalytic composition. Off to the combinations, the substance quantities share of the main components Nb was stochastically altered by means of ZG3 [with the help of the numerical random generators G05CAF and G05CCF of NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd, 1986)]. In a similar manner, we obtained K 2, 3, 6, 7 and 8 of the third catalyst generation (Table 3).

b) We proceeded exactly as in part (b) of step 7. We obtained K 4 and 5 of the third generation (Table 3). In a similar manner, we obtained K 9 and 10 of the third generation. The total resultant 10 new catalysts of the third generation are produced as in the case of the first and second generations (Steps 2 and 7).

Step 11. The 10 new catalysts of the third catalysts generation were produced according to directions (see step 1) and were tested parallel under standard conditions as described in step 4. (see above step (h)) Among the 10 new catalysts, we now find two (number 4 and number 9) with which the hitherto highest yields were exceeded. Thus catalysts number 4 and 19 (Table 1) are displaced from the first and second rank (see figure 1).

Step 12. The catalysts compositions of the next following generations (the nth generation) were selected similar to steps 6 - 8 or 9 - 11; each time the five best catalysts were selected from already examined catalysts generations and were used for the determination of the compositions of the 10 new catalysts of the nth catalysts generation (see above steps (i), (j), (k)).

Result: When the composition of the five best catalysts of the first to third catalysts generations are compared, it was found that all catalysts contain Mo, Sn, Co and carrier components. The qualitative of the three best catalysts are almost identical. All of these catalysts thus contain Mo, Nb, Sb, Sn, Co, Ga and the carrier component. The two best catalysts in addition also contain the doping components Cu and Pd. This clearly proves that the catalysts compositions approach each other with the progressing number of generations that is to say, disturbing components are no longer considered during the course of optimization and the components of the catalysts with high oxygenate yields on the other hand are increasingly considered during the determination of new catalyst compositions.

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In the third catalysts generation, on the basis on this evolutionary strategy, one encounters a 100% higher oxygenate exchange than in the first generation (Figure 1).

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Example 2

First of all 20 catalysts (Generation I), then 10 catalysts
(Generation II, III), and finally another 10 catalysts
(Generation IV) starting with 13 oxides, that were used as
primary catalysts component were prepared and were tested during
the oxidative dehydration of propane. The objective was to make
propane into propene with the highest possible yield and
selectivity via oxidative dehydration. The course of the
procedure comprises the following steps and leads to the
particular mentioned results.

The 1st Catalyst Generation

Step 1. The components were elected from among the oxides
of the elements V, Mo, Mn, Fe, Zn, Ga, Ge, Nb, W, Co, Ni, Cd,
In. The atomic shares of the individual elements in the
catalysts were varied between zero and 1. Each catalyst
contains three of the elements V, Mo, Mn, Fe, Zn, Ga, Ge, Nb, W,
Co, Ni, Cd, In. The sum of all atomic shares of these elements
always turns out to be 1.

Step 2. The catalysts compositions of the first
generation, obtained by means of ZG4 [numerical random
generators G05DZF, G05CAF, G05DYF, G05CCF of NAG-Bibliothek (NAG
FORTRAN Workstation Library, NAG Group Ltd. 1986)] are compiled
in table IV.

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Step 3. The catalysts, that we use for testing, were obtained by means of the following production methods: compounds

$(NH_4VO_3, (NH_4)_6Mo_7O_{24}\cdot 4H_2O, Mn(NO_3)_2\cdot 4H_2O, Fe(NO_3)_3\cdot 9H_2O,$

$Zn(NO_3)_2\cdot 6H_2O, Ga_2O_3, GeO_2, Nb_2O_5, H_2WO_4, Co(NO_3)_2\cdot 6H_2O, Ni(NO_3)_2\cdot 6H_2O,$

$Cd(NO_3)_2\cdot 4H_2O, In(NO_3)_3\cdot H_2O)$ der in Schritt 1 genannten Elemente

of the elements mentioned in step 1, were dissolved or washed in water were mixed with each other and the mixture was evaporated. The resultant solid was dried for ten hours at 120°C; it was then calcined in air for three hours at 600°C.

Table 4. Compilation of Catalyst of the First Generation

① Kat. No	Zusammensetzung ②	① Kat. No	Zusammensetzung ②
1/1	$Fe_{0.79}Ga_{0.02}Nb_{0.19}O_x$	1/11	$V_{0.47}W_{0.19}Ni_{0.33}O_x$
1/2	$Mo_{0.44}Ni_{0.23}In_{0.33}O_x$	1/12	$Mn_{0.41}Ga_{0.51}Nb_{0.08}O_x$
1/3	$Zn_{0.70}Ge_{0.00}Co_{0.22}O_x$	1/13	$Mo_{0.45}Co_{0.22}In_{0.33}O_x$
1/4	$V_{0.33}Fe_{0.43}Cd_{0.24}O_x$	1/14	$Fe_{0.75}Ge_{0.05}W_{0.20}O_x$
1/5	$Ga_{0.01}Nb_{0.33}Ni_{0.66}O_x$	1/15	$V_{0.33}Mn_{0.43}Ni_{0.23}O_x$
1/6	$Mo_{0.33}Zn_{0.42}In_{0.25}O_x$	1/16	$Zn_{0.67}Nb_{0.1}Co_{0.23}O_x$
1/7	$Ge_{0.11}W_{0.33}Cd_{0.56}O_x$	1/17	$Mo_{0.33}Fe_{0.42}Cd_{0.25}O_x$
1/8	$V_{0.26}Mn_{0.33}Ga_{0.41}O_x$	1/18	$Ga_{0.01}W_{0.33}Ni_{0.66}O_x$
1/9	$Nb_{0.16}Co_{0.33}In_{0.51}O_x$	1/19	$Mn_{0.33}Zn_{0.41}In_{0.25}O_x$
1/10	$Mo_{0.42}Ge_{0.44}Fe_{0.33}O_x$	1/20	$Ge_{0.14}Co_{0.33}Cd_{0.53}O_x$

KEY:

Kat. No - catalyst Number

Zusammensetzung - Composition

Step 4. The catalysts were tested parallel in 6 quartz reactors (inside diameter 6 mm) that were inserted in a heatable and coolable fluidized sand bed for thermostat control. The following standard experimental conditions were chosen for

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testing the catalysts: T=500°C, $m_{catalyst}$ = 0.3g, $C_3H_8/O_2/N_2$ = 2/1/2, $V_{total\ per\ reactor}$ – became variant between 10 and 100 ml/min (STP). The catalysts were used for the reaction and were tested for the propane mixtures and propene selections obtained with the mentioned experimental conditions (see step (b) above). The concentration of propane, propene, ethylene, methane and the developing oxygen derivatives as well as of CO and CO_2 was analyzed by means of gas chromatograph.

Step 5. Table 5 illustrates the results of testing the first generation of catalysts (propane mixture, propene selectivity and propene yield). Significant differences develop in the yields within the 20 tested catalysts and these yields are a product of the mixture and the selectivity. Four catalysts (Numbers 1/4, 1/8, 1/10, 1/15) showed the best results for catalytic mixing. /20

Table 5. Catalytic Results of the First Generation

Tabelle 5. Katalytische Ergebnisse der ersten Generation

Kat.-Nr. ①	Zusammensetzung ②	$X(C_3H_8)$ %	$S(C_3H_6)$ %	$Y(C_3H_6)$ %
1/1	$Fe_{0.79}\ Ga_{0.02}\ Nb_{0.19}$	10.7	17.7	1.9
1/2	$Mo_{0.44}\ Ni_{0.23}\ In_{0.33}$	11.8	14.3	1.7
1/3	$Zn_{0.70}\ Ge_{0.08}\ Co_{0.22}$	20.3	0.04	0.01
1/4	$V_{0.33}\ Fe_{0.43}\ Cd_{0.24}$	15.3	24.5	3.7
1/5	$Ga_{0.01}\ Nb_{0.33}\ Ni_{0.66}$	8.9	2.5	0.2
1/6	$Mo_{0.33}\ Zn_{0.42}\ In_{0.25}$	1.3	26.2	0.3
1/7	$Ge_{0.11}\ W_{0.33}\ Cd_{0.56}$	0.2	15.6	0.03
1/8	$V_{0.26}\ Mn_{0.33}\ Ga_{0.41}$	6.9	43.4	3.0
1/9	$Nb_{0.16}\ Co_{0.33}\ In_{0.51}$	15.2	12.1	1.8
1/10	$Mo_{0.03}\ Ge_{0.44}\ Fe_{0.53}$	6.3	35.1	2.2
1/11	$V_{0.47}\ W_{0.19}\ Ni_{0.33}$	44.6	2.3	1.0
1/12	$Mn_{0.41}\ Ga_{0.51}\ Nb_{0.08}$	13.1	12.7	1.7
1/13	$Mo_{0.43}\ Co_{0.22}\ In_{0.35}$	1.0	46.5	0.5
1/14	$Fe_{0.75}\ Ge_{0.05}\ W_{0.20}$	16.0	12.9	2.1
1/15	$V_{0.33}\ Mn_{0.43}\ Ni_{0.23}$	12.5	26.6	3.3
1/16	$Zn_{0.67}\ Nb_{0.1}\ Co_{0.23}$	15.2	0.3	0.05
1/17	$Mo_{0.33}\ Fe_{0.42}\ Cd_{0.25}$	2.1	7.7	0.2
1/18	$Ga_{0.01}\ W_{0.33}\ Ni_{0.66}$	23.6	3.3	0.8
1/19	$Mn_{0.33}\ Zn_{0.41}\ In_{0.25}$	15.7	9.5	1.5
1/20	$Ge_{0.14}\ Co_{0.33}\ Cd_{0.53}$	14.6	8.6	1.3

KEY:

Kat. no – catalyst number

Zusammensetzung – composition

2nd Catalyst Generation

Step 6.   The 2nd Generation of catalysts of obtained in the following manner: first of all, the 4 catalysts (Numbers. 4, 8, 10, 15) with the best catalytic behavior were selected and were used for further modification.

Step 7.   The compositions of the new catalysts 2/21 of the 2nd generation was obtained in a manner similar to the description given in step 7 in Example 1 starting with K 1/15 and the main component V, then K 1/8 and the main component Ga, then K 1/4 and the main component Cd, then K 1/10 and the

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secondary component Ge.   The components thus selected were combined with their original molar quantities to form a new catalyst composition.   The catalysts 2/22 to 2/30 of the 2nd generation were obtained in a similar manner.   All of the resultant 10 new catalyst of the second generation were produced as those of the first generation (step 2).

Step 8.   The procedure described in Step 7, was used to determine 10 new catalysts compositions, and were made according to instructions (see step 3) and they were tested parallel under standard conditions as described in step 4 (see step (e) above).

The results are compiled in Table 6.

Table 6. Composition and catalysts results of the 2nd Generation

① Kat.-Nr.	② Zusammensetzung	$X(C_3H_8)$ %	$S(C_3H_6)$ %	$Y(C_3H_6)$ %
2/21	$V_{0.33}Ga_{0.40}Cd_{0.23}Ge_{0.04}O_x$	2.4	54.0	1.3
2/22	$V_{0.30}Fe_{0.49}Ni_{0.21}O_x$	26.1	1.4	0.4
2/23	$V_{0.30}Fe_{0.48}Cd_{0.22}O_x$	13.8	20.2	2.8
2/24	$V_{0.67}Mn_{0.22}Ga_{0.11}O_x$	17.0	37.0	6.3
2/25	$Mo_{0.45}Fe_{0.25}Ge_{0.29}O_x$	0.2	66.9	0.1
2/26	$Fe_{0.09}Ge_{0.33}Ni_{0.58}O_x$	16.7	1.8	0.3
2/27	$V_{0.26}Mo_{0.33}Fe_{0.41}O_x$	17.4	22.4	3.9
2/28	$Ga_{0.15}Ge_{0.33}Cd_{0.52}O_x$	2.7	6.2	0.2
2/29	$V_{0.43}Mn_{0.54}Fe_{0.03}O_x$	16.4	34.1	5.6
2/30	$V_{0.48}Ge_{0.19}Ni_{0.33}O_x$	43.1	0.4	0.2

KEY:

Kat. Nr – catalyst number

zusammensetzung – composition

3rd Catalyst Generation

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Step 9. From the catalysts of the first and second catalysts generation, we again selected 4 catalysts with the best output (Numbers 8, 24, 27, 29) (See step (f) above) and they were used as places for additional steps.

Step 10. The composition of 10 catalysts of the 3rd generation that were to be newly reproduced was obtained in the following manner: using the 4 catalysts selected in step 9, we proceeded as described in step 7 or in step 10 in example 1 (see Table 6, see step (g) above) starting with K 2/29 and the main component V, then K 2/27 and the main component Mo, then K 2/24 and the main component Mn. The components thus selected were combined with their original molar quantities to form a new catalyst composition. The catalysts 3/52 to 3/60 of the third generation were obtained in a similar manner (Table 7). The total resultant 10 new catalysts of the third generation were produced as those of the first and second generations (steps 2 and 7).

Step 11. The 10 new catalysts of the 3rd catalyst generation were made according to instructions (see step 3) and were tested parallel under standard conditions as described in step 4. (see step (h) above)

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Table 7. Compositions and catalytic results of the third generation

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① Kat. Nr.	Zusammensetzungen ②	$X(C_3H_8)/\%$	$S(C_3H_6)/\%$	$Y(C_3H_6)/\%$
3/51	$V_{0.32}$ $Mo_{0.41}$ $Mn_{0.27}$	13.6	28.4	3.9
3/52	$V_{0.26}$ $Mn_{0.33}$ $Ga_{0.41}$	20.4	29.9	6.1
3/53	$V_{0.20}$ $Mn_{0.17}$ $Fe_{0.34}$ $Ga_{0.32}$	19.7	39.0	7.7
3/54	$V_{0.47}$ $Mn_{0.13}$ $Ga_{0.38}$	19.8	31.9	6.3
3/55	$V_{0.17}$ $Mn_{0.22}$ $Fe_{0.61}$	19.2	31.5	6.0
3/56	$Mn_{0.15}$ $Fe_{0.33}$ $Ga_{0.52}$	13.9	6.7	0.9
3/57	$V_{0.43}$ $Mo_{0.54}$ $Mn_{0.03}$	14.8	33.8	5.0
3/58	$Mo_{0.48}$ $Fe_{0.10}$ $Ga_{0.33}$	2.2	59.8	1.3
3/59	$V_{0.42}$ $Mo_{0.52}$ $Mn_{0.07}$	17.6	28.8	5.1
3/60	$V_{0.46}$ $Fe_{0.21}$ $Ga_{0.33}$	17.4	33.5	5.8

KEY:

Kat. nr - catalyst number

zusammensetzungen - compositions

4th Catalyst Generation

4th Catalyst Generation

Step 12. From among the catalyst of the 1st to 3rd catalysts generations, we again chose 4 catalysts with the best performance (Numbers 24, 53, 54, 55) (see Step (f) above) and we used them as basis for the new catalysts of the 4th generation.

Step 13. The composition of 10 catalysts of the 4th generation that were to be newly produced was obtained in the following manner: we proceeded as in step 7 with the 4 catalysts selected (see table 7, see step (g) above).

Step 14. The 10 new catalysts of the 3rd catalyst generation were made according to directions (see step 3). And were tested parallel under standard conditions described in step 4 (see Step (h) above).

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A definite increase in the propene yield is achieved according to figure 2 already with the 4th generation.

Table 8. Compositions and results of the 4th Generation

① Kat. Nr.	Zusammensetzung ②	X(C$_3$H$_8$) %	S(C$_3$H$_6$) %	Y(C$_3$H$_6$) %
4/71	V$_{0.40}$ Mn$_{0.14}$ Ga$_{0.38}$	18.6	39.4	7.3
4/72	V$_{0.53}$ Mn$_{0.14}$ Fe$_{0.34}$	18.8	27.1	5.1
4/73	V$_{0.32}$ Fe$_{0.27}$ Ga$_{0.27}$	21.7	32.9	7.1
4/74	V$_{0.19}$ Mn$_{0.24}$ Fe$_{0.32}$ Ga$_{0.25}$	22.3	35.9	8.0
4/75	V$_{0.06}$ Mn$_{0.02}$ Ga$_{0.92}$	22.2	34.6	7.7
4/76	Mn$_{0.5}$ Fe$_{0.16}$ Ga$_{0.33}$	21.6	32.6	7.0
4/77	V$_{0.42}$ Mn$_{0.53}$ Ga$_{0.04}$	9.7	34.1	3.3
4/78	V$_{0.47}$ Fe$_{0.19}$ Ga$_{0.33}$	22.2	33.0	7.3
4/79	V$_{0.41}$ Mn$_{0.51}$ Fe$_{0.08}$	12.6	22.1	2.8
4/80	V$_{0.45}$ Fe$_{0.22}$ Ga$_{0.33}$	20.9	33.4	7.0

KEY:

Kat. nr – catalyst number

zusammensetzung – composition

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Table 1   1st Catalyst Generation

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Tabelle 1.

1. Katalysatorgeneration

Column groups (② Zusammensetzung Mol-%): ③ Hauptkomponenten (V, Mo, Nb, Bi) · Nebenkomponenten (P, Mn, Sb, Sn, B) · ④ Dotierungen (Fe, Co, Cs, Ag, ⑤ Cu, Ga, In) · ⑥ Wasser (Ma-%) · Pd (Ma-%) · ⑦ Ausbeute an C₃-Oxygenaten (Mol-%) · ⑧ Rang unter den 5 besten Katalysatoren - Generation (1 2 3)

① Nr.	V	Mo	Nb	Bi	P	Mn	Sb	Sn	B	Fe	Co	Cs	Ag	Cu	Ga	In	Wasser Ma-%	Pd Ma-%	Mol-%	Rang 1	Rang 2	Rang 3
1	13,75	6,75	0	0	0	16,84	9,83	0	2,83	0,344	0	0	0	0	0	0	50	0,0001	0,000			
2	40,48	22,76	0	5,05	30,57	0	0	0	0	0	0	0	0	0	0	1,137	0	0,0001	0,000			
3	0	20,83	2,97	0	28,73	0	10,85	23,60	0	0	0	0	0,449	0	0	0	0	0,0001	0,034			
4	0	15,12	4,96	0	0	0	19,60	9,44	0	0	0,887	0	0	0	0,340	0	50	0	0,430	1.	1.	3.
5	8,59	0	0	0	0,230	23,87	13,26	0	2,65	0,448	0	0,707	0,173	0	0	0	50	0,0001	0,005			
6	11,04	38,88	0	19,56	0	0	0	0	28,07	0,761	0	1,63	0	0	0	0,595	0	0	0,000			
7	0	0	29,53	12,88	0	36,86	20,22	0	0	0	0	0	0	0	0,372	0	0	0	0,025			
8	11,96	38,26	0	0	20,00	0	1,74	28,04	0	0,463	0	0,748	0,843	0	0	0	50	0,0001	0,007			
9	0	9,09	22,49	0	0	0	13,19	3,88	0	0,218	0	0,305	0,262	0	0	0,610	50	0	0,039			
10	10,14	0	1,54	13,93	0	0	5,33	0	17,72	1,232	0	0,410	0,987	0,467	0,763	0	50	0,0001	0,024			
11	0	0	0	6,09	0	0	29,09	0	13,12	0,287	0	0,398	0,607	0	0	0,427	50	0	0,011			
12	0	0	0	18,37	6,77	0	0	15,20	23,48	0	0	0	0	0	0	0,986	0	0,0001	0,030			
13	0	6,69	34,53	0	0	0	0	0	43,04	0,321	0	0,548	0	0	0	0	50	0	0,082	4.		
14	0	11,33	4,54	0	14,33	7,53	0,73	2,70	10,53	0	0	0,668	0,226	0	0	0,343	50	0,0001	0,016			
15	0	20,09	11,40	0	0	0	0	0	15,23	0	0	0,582	0	0	0	0	0	0	0,053			
16	10,37	1,67	0	14,20	5,50	0	0	18,04	0	0	0,222	0,198	0	0,435	0,166	0	50	0	0,045			
17	8,56	2,90	0	11,06	5,40	0	0	13,55	7,89	0	0	0,495	0	0	0	0,340	50	0,0001	0,077	5.		
18	14,11	0	5,89	17,74	13,48	0	9,51	1,28	0	0,318	0,466	0	0	0,452	0,700	0	50	0	0,011			
19	0	9,11	0	23,40	20,33	0	0	3,56	25,66	0	0	0,318	0	0	0	0	50	0,0001	0,215	2.	2.	4.
20	27,10	15,00	0	2,90	18,58	0	0	8,23	24,25	0	0	0,393	0	0	0	0	50	0,0001	0,015			
21	0	0	0,187	0	0	5,69	20,21	0	0	0	1,069	0	0,939	0	0	0	0	0	0,085	3.	5.	
22	0	0	29,61	12,82	0	37,00	55,66	0	0	1,723	0,353	1,652	0	0	0	0	0	0	0,001			
23	0	0	0	39,59	12,47	3,10	0	0	0	0	0	0	0	0	0,345	0	0	0,0001	0,001			
24	20,70	5,98	0	27,18	7,13	33,67	42,87	18,06	0	0	0	0,801	0	0	0	0	0	0	0,005			
25	0	0	0	31,94	0	0	0	0,94	28,17	0	0	0	0	0	0,474	0	0	0,0001	0,018			
26	11,51	17,04	38,74	19,84	2,67	0	0	11,02	0	0	0,531	0	0	0	0	0	0	0,0001	0,002			
27	6,69	9,24	0	9,85	28,46	0	0	1,77	21,00	0	0,659	0,328	0	0,454	0,691	0	50	0,0001	0,014			
28	22,58	0	0	0	11,41	15,12	2,87	15,17	0	0	0	0	0	0	0	0,208	0	0,0001	0,000			
29	0	0	19,95	0	19,45	0	0	1,73	0	0	0	0,597	0	0	0,240	0	50	0,0001	0,004			
30	29,36	11,64	0	37,17	0	0	0	0	0	0	0,649	0	0	0	1,001	0	0	0	0,002			

KEY:

Nr – number

Zusammensetzung Mol % – % by Mol composition

Hauptkomponenten – main components

nebenkomponenten – secondary components

Dotierungen – dopings

trager- carrier

Ausbeute en C_3-Oxygenaten – yield of C_3-Oxygenates

Rang unter den 5 besten katalysatoren – Rank among the 5 best
catalysts   /24

Table 2. 2nd Catalyst Generation

Tabelle 2.

2. Katalysatorgeneration

Zusammensetzung Mol-%

Nr	Hauptkomponenten					Nebenkomponente				Dotierungen							Träger Ma-%	Pd Ma-%	Ausbeute an C₃-Oxygenaten Mol-%	Rang unter den 5 besten Katalysatoren Generation 2	3
	V	Mo	Nb	Bi	P	Mn	Sb	Sn	B	Fe	Co	Cs	Ag	Cu	Ga	In					
1	0	0	0	8.54	14.34	0	0	7.28	18.72	0.83	0.825	0.303	0	0	0	0	50	0.0001	0.037		
2	0	10.82	0	0	22.07	0	0	16.10	0	0.55	0.553	0.467	0	0	0	0	50	0.0001	0.184	3.	
3	0	15.47	0	0	19.01	0	0	13.87	0	0	0.908	0.402	0	0	0.325	0	50	0	0.161	4.	
4	0	2.87	15.14	0	0	0	26.50	4.22	0	0	0.738	0	0	0	0.536	0	50	0.0001	0.001		
5	0	11.79	0	11.48	1.35	0	0	24.43	0	0	0.952	0	0	0	0	0	50	0.0001	0.024		
6	0	4.37	3.24	7.22	12.13	0	12.80	9.93	0	0	0.300	0	0	0	0	0	50	0.0001	0.020		
7	0	0	0	0	26.54	0	0	21.71	0	0	1.270	0	0	0	4.810	0	50	0.0001	0.024		
8	6.42	6.82	0	0	13.92	4.27	0	11.39	5.91	0	0.670	0.150	0	0.330	0.120	0	50	0.0001	0.000		
9	0	4.04	9.23	0	0	0	20.15	13.75	0	0	2.090	0	0	0	0.740	0	50	0.0001	0.003		
10	0	3.09	0	26.10	5.85	0	0	13.69	0	0	1.270	0	0	0	0	0	50	0.0001	0.000		

KEY:

Nr — number

Zusammensetzung Mol % - % by Mol composition

Hauptkomponenten — main components

nebenkomponenten – secondary components

Dotierungen – dopings

trager- carrier

Ausbeute en C_3-Oxygenaten – yield of C_3-Oxygenates

Rang unter den 5 besten katalysatoren – Rank among the 5 best catalysts /25

Table 3 3rd Catalyst Generation

Tabelle 3. 3. Katalysatorgeneration

Nr. (Ns) ①	Zusammensetzung Mol-% ②																Träger Ma-%	Pd Ma-%	Ausbeute an C₇-Oxygenaten Mol-% ⑥	Rang unter den 5 besten Katalysatoren ⑦
	Hauptkomponenten ③					Nebenkomponente				Dotierungen ⑤										
	V	Mo	Nb	Bi	P ④	Mn	Sb	Sn	B	Fe	Co	Cs	Ag	Cu	Ga	In				
1	0	0	31,78	0	17,10	0	0	0	0	0	0,82	0	0	0	0,31	0	50	0,0001	0,006	
2	0	6,34	24,05	0	12,94	0	0	0	5,50	0	0,62	0,14	0	0,30	0,12	0	50	0,0001	0,096	
3	0	6,40	14,62	9,90	0	0	0	0	18,22	0	0,38	0,23	0	0,12	0,07	0	50	0	0,010	
4	0	34,61	0,87	0	0	0	5,37	8,28	0	0	0,43	0	0	0,07	0,45	0	50	0,0001	0,821	2.
5	0	19,45	0	13,27	2,67	0	0	13,64	0	0	0,96	0	0	0,45	0	0	50	0,0001	0,035	
6	0	5,94	4,40	9,82	0	0	17,40	12,03	0	0	0,41	0	0	0	0,51	0	50	0,0001	0,000	
7	0	0	7,47	0	20,29	0	0	20,40	0	0	1,34	0	0	0	0,16	0	50	0,0001	0,050	
8	0	8,70	4,74	0	12,88	0	0	14,33	7,54	0	0,85	0,19	0	0,51	1,20	0	50	0,0001	0,161	
9	0	17,74	4,63	0	0	0	15,86	10,15	0	0	0,43	0	0	0,16	0	0	50	0,0001	0,965	1.
10	0	1,66	0	31,55	7,22	0	0	9,00	0	0	0,56	0	0	1,20	0	0	50	0,0001	0,063	

KEY:

Nr – number

Zusammensetzung Mol % - % by Mol composition

Hauptkomponenten - main components

nebenkomponenten - secondary components

Dotierungen - dopings

trager- carrier

Ausbeute en C_3-Oxygenaten - yield of C_3-Oxygenates

Rang unter den 5 besten katalysatoren - Rank among the 5 best

catalysts   /26

CLAIMS

1. Process for the production of active or selective solid catalysts from inorganic or organometallic substances from mixtures thereof through selection of a certain number of solid catalysts that are differently composed in chemical terms for quantitatively or chemically and quantitatively and determination of essential catalysts properties characterized in that for a certain catalytic reaction among the catalysts of the first generation that are best with respect to activity or selectivity, the individual catalyst components or substance quantities of the catalyst components or catalyst components and substance quantities are newly structured arbitrarily or randomly by means of stochastic methods, the activity or selectivity or activity and selectivity of the resultant catalyst of the 2nd Generation is determined among the best catalyst of the 2nd Generation, once again, a portion is newly

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structured arbitrarily or randomly by means of stochastic methods regarding the individual catalysts components or substance quantities of the catalysts components or catalyst components and substance quantities, the activity or selectively or the activity and selectivity of the resultant catalysts of the 3rd Generation is determined and these steps of new structuring from the best catalysts of all generations and the quality determination are determined until one gets one or several catalysts with qualities that are desirable for the specific catalytic reaction.

2. Process for the production of active or selective solid catalysts according to claim 1 characterized in that

a) for a catalytic reaction, a number n_1 of solid catalysts are made that exist in the form of compounds according to the following formula

$$(A^I_{a_I} .. A^i_{a_i})-(B^I_{b_I} .. B^j_{b_j})-(D^I_{d_I} .. D^k_{d_k})-(T^I_{t_I} .. T^I_{t_I})-O_p$$
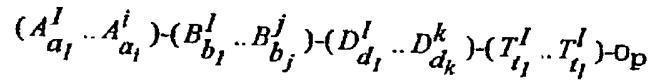
where,

A^1. . A^i are a number i of different main components that are selected from the group of elements of the PSE except for the transuranes and noble gases and the number i is between 1 and 10,

B^1. . B^j are a number j of different secondary components that

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are selected from the group of elements

and Nd and the j is between 1 and 10,

D^1. . D^k are a number k of different doping elements that are

selected from the group of elements

and Nd and the number k is between 1 and 10.

T^1. . T^l is a number l with different carrier components that

consists of oxides, carbonates, carbides, nitrides, boride of

the elements Mg, Ca, Sr, Ba, La, Zr, Ce, Al, Si or a mixing

phase of two or several thereof and the number l is between 1

and 10,

and the O is Oxygen,

a_1 . . a_i are identical or different substance quantity shares of

0 to 100% by mol with the proviso that the substance quantity

shares a_1 . . a_i cannot all simultaneously be 0.

b_1 . . b_j are substance quantity shares of 0 to 90% by mol,

d_1 . . d_k are substance quantity shares of 0 to 10% by mol,

t_1 . . t_1 are substance quantity shares of 0 to 99.99% by mol, p is a substance quantity share of 0 to 75% by mol, where the sum of all substance quantity shares a_1 + b_j + d_k + t_1 must not be greater than 100% and the number n_1 of catalysts with a different composition in terms of quantity or in chemical terms or quantitatively and chemically is in the range of 5 to 100,000.

b) The activity or selectivity or activity and selectivity of the solid catalyst of the first generation made according to (a) are experimentally determined for a catalytic reaction and a reactor or in several parallel connected reactors;

c) from among the number of n_1 catalysts over the first generation, one selects a number of between 1 and 50% with the highest activities for a specific reaction or the highest selectivities for the desired product or product mixture of the catalytic reaction or activity and selectivity as the number n_2 ;

d) the catalyst components, contained in the number n_2 of catalysts, with a fixed probability W that results for each of the components A^1. . A^i , B^1. . B^j , D^1. . D^k and T^1. . T^1 from the corresponding equation

$$W_A = \frac{1}{i \cdot n_2} \cdot 100\%, W_B = \frac{1}{j \cdot n_2} \cdot 100\%, W_D = \frac{1}{k \cdot n_2} \cdot 100\%, W_T = \frac{1}{l \cdot n_2} \cdot 100\%$$

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are exchanged between 2, each catalysts selected from the
quantity n_2 with a probability of

$$W_{Kat} = \frac{1}{n_2} \cdot 100\%$$

or that substance quantities a_1 . . a_i, b_1 . . b_j, d_1 .
. d_k and t_1 . . t_l of the catalysts components A^1 . . A^i , B^1 . . B^j ,
D^1 . . D^k and T^1 . . T^l are varied with some of the catalysts
selected with the probability

$$W_{Kat} = \frac{1}{n_2} \cdot 100\%$$

in that new values are determined for the substance
quantities shares a_1 . . a_i, b_1 . . b_j, d_1 . . d_k and t_1 . . t_l
within the boundaries defined in (a) or that exchange and
variation are performed;

in this way, one produces new catalysts having the general
formula (I) with the meaning – mentioned in (a) – of A, B, D, T,
a, b, d, t and p in a number y_2 that perform the second
generation of catalysts;

e) the activities or selectivities or activities and
selectivities of the y_2 solid catalyst of the second generation
are determined experimentally for the same specific reaction as
in (b) in one or several reactors;

f) a number of n_3 solid catalysts of the second generation are
selected, these having the highest activities for the catalytic
mixing or the highest selectivities for the desired product and
product mixture for activities and selectivities from all solid

catalysts of the first and second generations where the number n_3 corresponds to between 1 and 50% of the number n_1;

g) the catalysts components contained in the number n_3 of catalysts are exchanged with a fixed probability W that results for each component A^1. . A^i , B^1. . B^j , D^1. . D^k and T^1. . T^1 from the corresponding equations:

$$W_A = \frac{1}{i \cdot n_3} \cdot 100\%, \; W_B = \frac{1}{j \cdot n_3} \cdot 100\%, \; W_D = \frac{1}{k \cdot n_3} \cdot 100\%, \; W_T = \frac{1}{l \cdot n_3} \cdot 100\%$$

between 2 each, catalysts selected with a probability of

$$W_{Kat} = \frac{1}{n_3} \cdot 100\%$$

from the quantity n_3 or that the substance quantities a_1 . . a_i, b_1 . . b_j, d_1 . . d_k and t_1 . . t_1 of the catalysts components A^1. . A^i , B^1. . B^j , D^1. . D^k and T^1. . T^1 are varied for some of the catalysts selected with the probability

$$W_{Kat} = \frac{1}{n_3} \cdot 100\%$$

in that new values are determined for the substance quantity shares a_1 . . a_i, b_1 . . b_j, d_1 . . d_k and t_1 . . t_1 within the boundaries defined in (a) or that exchange and variation are performed;

in this manner, one produces new catalysts having the general formula (I) with the meaning – given in (a) – of A, B, D, T, a, b, d, t and p in a number y_3 that form the third generation of catalysts;

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h) the activity or selectivity or activity and selectivity of the y_3 new catalysts of the third generation made according to (g), is determined [sic] for the same specific reaction as mentioned in (b) in one or several reactors;

i) a number of solid catalysts of the nth generation that display the highest activities for the catalytic mixing or the highest selectivity for the desired product and product mixture or activity and selectivity from all solid catalysts of the first to nth generation, where the number n_{n+1} corresponds to be between 1 and 50% of the number n_1;

j) the catalysts components contained in the number n_{n+1} of catalysts with a fixed probability W that results from each of the components A^1. . A^i, B^1. . B^j, D^1. . D^k and T^1. . T^l from the corresponding equations /30

$$W_A = \frac{1}{i \cdot n_{n+1}} \cdot 100\%, W_B = \frac{1}{j \cdot n_{n+1}} \cdot 100\%, W_D = \frac{1}{k \cdot n_{n+1}} \cdot 100\%, W_T = \frac{1}{l \cdot n_{n+1}} \cdot 100\%$$

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are exchanged with 2 each catalysts chosen from the quantity n_{n+2} with a probability of

$$W_{Kat} = \frac{1}{n_{n+1}} \cdot 100\%$$

or that the substance quantities a_1 . . a_i, b_1 . . b_j, d_1 . . d_k and t_1 . . t_l of the catalysts components A^1. . A^i, B^1. . B^j, D^1. . D^k and T^1. . T^l are varied for some catalysts selected for the probability

$$W_{Kat} = \frac{1}{n_{n+1}} \cdot 100\%$$

in that one determines new values for the substance quantity

shares a_1 . . a_i, b_1 . . b_j, d_1 . . d_k and t_1 . . t_l

within the boundaries defined in (a) or that exchange and

variation are performed;

in this fashion, one makes new catalysts having the general

formula (I) with the meaning given in (a) – of A, B, D, T, a, b,

d, t and p in a number y_{n+1} that form the $(n+1)^{th}$ generation of

catalysts;

k)   the activity or selectivity or activity and selectivity of

the y_{n+1} new catalysts of the $(n+1)^{th}$ generation made according to

(g) is determined for the same reaction as in (b) in one or

several reactors;

l)   the   selection   according   to   steps   (c)+(f)+(i),   the

production of a new catalysts generation according to steps (d),

(g),   (j)   and   the   activity/selectivity   determination   are

continued according to steps (e)+(h)+(k) until one obtains a

catalyst   generation   where   the   activity   or   selectivity   or

activity and selectivity is/are not or no longer significantly

increased when compared to the preceding generation in terms of

the arithmetic mean.

3.   Process according to claim 2 characterized in that the

exchange   of   catalysts   or   the   variation   of   the   substance

quantities or the exchange and variation is/are performed in sections (d), (g) and (j) by means of a numerical random generator. /$\underline{31}$

4. Process according to claim 3 characterized in that the program codes G05CAF, G05DYF, G05DZF and G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd. 1986) of a numerical random generator are used.

5. Process according to 2(a) characterized in that the number n_1 of catalysts whose composition differs quantitatively or chemically or quantitatively and chemically is within the range of 5 to 100.

6. Process according to claim 2 characterized in that the selection number n_2, n_3, or n_{n+1} corresponds to between 5 and 30% of the number n_1.

7. Process according to claim 2 characterized in that the main components are selected from the group consisting of

Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce und Nd.

and Nd.

8. Process according to claim 2 characterized in that the substance quantity shares b_1 . . b_j amount to between 0 and 50% by mol.

9. Process according to claim 2 characterized in that the catalysts mixtures are made by mixing salt solutions of the elements of the component A^1 . . A^i , B^1 . . B^j , D^1 . . D^k and T^1 . . T^l and that this is followed up by thermal treatment in the presence of the reactive or inert gas phase (tempering) or by means of joint precipitation of compounds that are difficult to dissolve and subsequent tempering or by impacting carrier components T^1 . . T^l with salt solutions or gaseous compounds of the components A^1 . . A^i , B^1 . . B^j , D^1 . . D^k and subsequent tempering where the employed salts can be nitrates, sulfates, phosphates, carbonates, halogenides, oxalates, carboxylates or mixtures thereof or carbonyls or acetylacetonates.

10. Process according to claim 2 characterized in that the catalytic reaction is performed with liquid, evaporated, or gaseous reactants.   /32

11. Process according to claim 2 characterized in that the reactants for the catalytic reaction are supplied to several reactors and that the product flow, leaving the reactors, is separately analyzed for each individual reactor.

12. Process according to claim 11 characterized in that – to perform the catalytic reaction – one connects parallel to each other between 5 and 1000 reactors consisting of spaces with catalytically active material arranged therein or are arranged

in arrays and that the diameters of these spaces amount to 100 µm to 10 mm and that the length are between 1 mm and 100 mm.

13. Process according to claim 11 characterized in that considering the specified reactor length, the throughput of the reactants is so chosen that the desired degree of mixing is obtained.

14. Process according to claim 11 characterized in that as reactor one uses a monlith with many parallel channels, that optionally can be closed off on the entry or exit side individually, or in larger numbers also during the catalytic reaction, or are a porous module preferably with channels running parallel in the direction of flow of the reaction mixture that can optionally be closed on the entry or exit side individually or in larger numbers also during the catalytic reaction.

15. Process according to claim 1 characterized in that the reactants for the catalytic reaction are supplied to the reactors designed according to claim 11, 12, and 13 and that the composition of the product flows, leaving the reactors, is analyzed by a measurement probe where the measurement probe is guided in a two-dimensional manner over the exit cross-sections of all the reactors or where the reactors are moved in a two-dimensional manner with respect to the measurement probe and the

part of the product flows, acquired by the measurement probe is

supplied to the analyzer.   /33
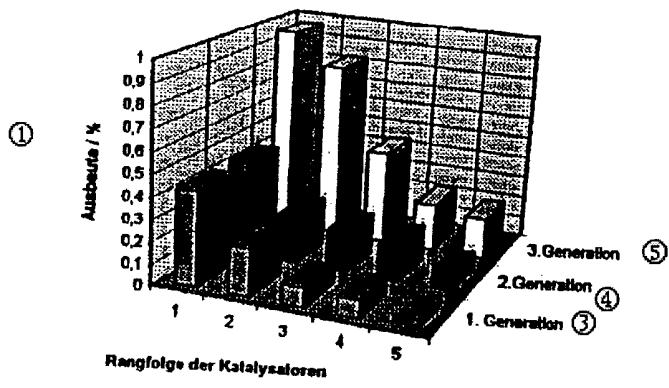
Fig. 1

KEY:

Ausbeute – yield

Rangfolge der Katalysatoren – ranking of catalyst

1. generation – first generation

2. generation – second generation

 3. generation – third generation
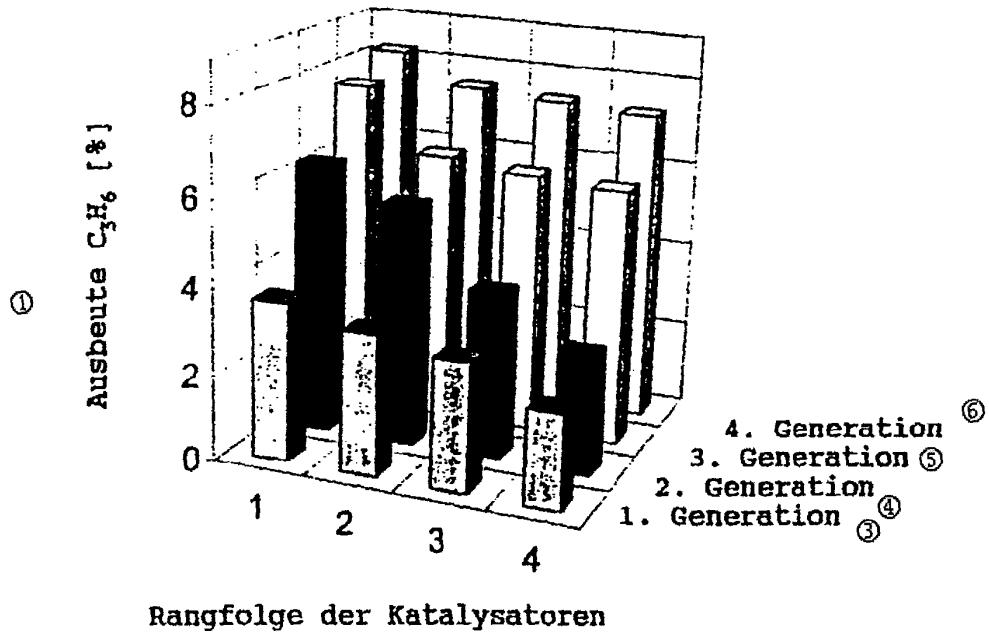
Fig. 2

KEY:

Ausbeute - yield

Rangfolge der Katalysatoren - ranking of catalyst

1. generation - first generation

2. generation - second generation

3. generation - third generation

4. generation - forth generation